Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Research Bulletin 40 (2005) 341–345
Materials Research Bulletin
www.elsevier.com/locate/matresbu

# Mechanochemical synthesis of $NaNbO_3$

Tadej Rojac*, Marija Kosec, Barbara Malič, Janez Holc

*Jozef Stefan Institute, Electronic Ceramics Department, Jamova 39, 1000 Ljubljana, Slovenia*

Received 28 July 2004; accepted 21 October 2004

**Abstract**

The mechanochemical synthesis of $NaNbO_3$ is studied. It is shown that $NaNbO_3$ can be prepared by milling the constituents, i.e. $Na_2CO_3$ and $Nb_2O_5$ in the planetary mill. After 40 h of mechanochemical treatment $NaNbO_3$ nanoparticles in the range of 10–20 nm are obtained. Furthermore, the high-energy milling leads to the mechanochemically-triggered carbonate decomposition, which has been observed for a few cases in the open literature.


*Keywords:* A. Oxides; C. Electron microscopy; C. X-ray diffraction

## 1. Introduction

Sodium niobate ($NaNbO_3$) is of great interest because it exhibits a number of phase transitions between paraelectric, antiferroelectric and ferroelectric phases [1–4]. When mixed with a small amount of $KNbO_3$ (0.6 at.% of K or $K_{0.006}Na_{0.994}O_3$), $NaNbO_3$ becomes ferroelectric and shows an improvement in its piezoelectric properties [5]. A broad peak in the piezoelectric properties was also observed close to the $K_{0.5}Na_{0.5}NbO_3$ (KNN) composition [6,7]. Furthermore, it has been shown that the addition of $LiNbO_3$ to $NaNbO_3$ produces a ferroelectric phase [8,9]. For this reason, $NaNbO_3$ has shown an increasing interest due to its role in the production of lead-free piezoelectric ceramics.

The conventional processing of alkaline niobate powders usually involves multiple steps of phase-forming calcination at high temperatures, which can lead to the volatilisation of alkaline species and, as a result, the formation of undesirable secondary phases. Furthermore, agglomerates are often formed

* Corresponding author. Tel.: +386 1 477 38 34; fax: +386 1 426 31 26.
*E-mail address:* tadej.rojac@ijs.si (T. Rojac).

0025-5408/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2004.10.018

during heating, which can adversely affect the sinterability of the resulting powder. In order to avoid such drawbacks, a mechanochemical route can be employed to synthesize the $NaNbO_3$ using alkaline carbonates and niobium (V) oxide as the starting compounds.

Mechanochemical synthesis was originally developed for the production of alloys and intermetallic compounds in 1966 [10]. Its major advantage is that the solid-state reaction is activated by the mechanical energy rather than the calcination at elevated temperatures. Since the mechanochemical technique has shown an increasing interest for the synthesis of complex ceramic oxides, great efforts have been made in order to understand the basic principles and the mechanisms involved. Recently, attention has been paid to the influence of different starting compounds, i.e., oxides, hydroxides and carbonates, on the course of the mechanochemical reactions during milling. It has been shown to be possible to synthesize a variety of feroelectric materials, such as $PbTiO_3$ (PT) [11], $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [12], $Pb(Sc_{0.5}Ta_{0.5})O_3$ (PST) [13] and $SrBi_4Ti_4O_{15}$ (SBIT) [14] using a single-step mechanochemical technique and starting from oxide precursors. In addition, a novel soft mechanochemical procedure has been developed by Senna [15] using a mixture of oxides and hydroxides as the starting compounds. In this case the mechanochemical reaction proceeds via a superficial acid/base mechanism, which allows a reduction in the subsequent synthesis temperature to a lower expence of mechanical energy.

Several attempts have been made to synthesize various complex oxides using mechanochemical synthesis starting from a powder mixture of carbonates and oxides, such as $BaTiO_3$ [16–20], $SrTiO_3$ [21], $Sr_2TiO_4$ [21], $Sr_3Ti_2O_7$ [22], $SrFeO_{2.5}$ [23], $LiFeO_2$ [24], $(Ba_xSr_{1-x})TiO_3$ $(0 < x < 1)$ [25] and $BaAl_2Si_2O_8$ [26]. No formation of the final products was observed during the mechanochemical treatment. However, in all the cases the mechanical activation of the starting compounds enhances the reactivity of the as-milled powders and decreases the synthesis temperature. In contrast, Miloševic and co-workers [27,28] reported the mechanochemical formation of $Na_2SeO_3$ starting from a mixture of $Na_2CO_3$ and $SeO_2$. Similar observations were made for $LiMn_2O_4$ synthesis, where $LiCO_3$ reacts with $MnO_2$ almost completely [29]. On the other hand, no observable interaction between $Mn_2O_3$ and MnO with $Li_2CO_3$ occurs, showing the importance of the oxidation state of manganese on the course of the mechanochemical reaction.

Recently, a new synthesis route based on high-energy ball-milling has been applied to obtain $NaNbO_3$ from a starting powder mixture of $Na_2CO_3$ and $Nb_2O_5$ [30]. However, $NaNbO_3$ was not formed during milling. A prolonged milling (30 days) leads to the amorphization of the $Na_2CO_3$ and a reduction of the crystallite size. This in turn leads to the lowering of the temperature required for the completion of the reaction between $Na_2CO_3$ and $Nb_2O_5$ from 750 °C for the non-activated sample to 600 °C for the 30 days mechanochemically activated sample.

Here, we present the study of the mechanochemical synthesis of $NaNbO_3$ using $Na_2CO_3$ and $Nb_2O_5$ as the starting compounds. The aim of the work is to follow the course of the mechanochemical reaction between $Na_2CO_3$ and $Nb_2O_5$. The possibility to prepare $NaNbO_3$ by mechanochemical synthesis is discussed.

## 2. Experimental details

$Na_2CO_3$ (Alfa, 99.95–100.05%) and $Nb_2O_5$ (Alfa, 99.5%) were used as the starting compounds for the mechanochemical synthesis of $NaNbO_3$. Sodium carbonate powder was dried at 200 °C for 1 h prior to